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Safety of large-capacity lithium-ion battery and evaluation of battery system for telecommunications

Tomonobu Tsujikawa [a,*], Kahou Yabuta [a], Masayasu Arakawa [b], Koji Hayashi [c]

[a] NTT Facilities, Inc., 2-13-1, Kitaotsuka, Toshima-ku, Tokyo 170-0004, Japan
[b] NTT Facilities Research Institute Inc., 3-9-11 Midori-cho, Musashino-shi, Tokyo 180-8585, Japan
[c] Shin-Kobe Electric Machinery Co., Ltd., 1300 Yabata, Nabari-shi, Mie, 518-0493 Japan

HIGHLIGHTS

► The safety tests were performed based on the risks that can occur in communications.
► Flame retardant containing 200-Ah cell was significantly improved in safety.
► The 36 kW battery system consisted of developed modules and battery management system.
► The set battery can maintain a capacity equal to that of a single cell.

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ABSTRACT

In backup power sources for telecommunications equipment, it is desirable that the lithium-ion (Li-ion) cells have large capacity to minimize installation size of backup systems and to improve reliability of them by reducing a number of cells and accompanying protective devices. On the other hand, large-capacity Li-ion cell is difficult to manage safety problems. Therefore, safety improvement must be done to replace lead-acid batteries in conventional backup power sources. Improvement of lifetime has also to be achieved under the float-charging condition.

We have been developing large-capacity Li-ion cells of which safety are improved by adding phosphazene flame retardant. In this work, 200-Ahs cell is fabricated and several safety tests under the assumption of telecommunications backup use are carried out. The results show no explosion, ignition, or thermal runaway. Forced thermal runaway test of a cell in the module which involves 13 cells are also carried out. There is no explosion, ignition, or thermal runaway in other 12 cells. In addition, 36-kW Li-ion battery system consisted of the 200-Ahs cells and battery management system (BMS). The system was operated for about 400 days in a state of floating charge. More than 95% of initial capacity is obtained.

1. Introduction

Recent growth of information and communication technology and spread of next generation networks will accelerate the growth of large-capacity and high-speed data communication, and high quality extra information services will be offered in various fields. On the other hand, large-capacity and high-speed data communication needs the great increase of power consumption in communication equipments. That means it is necessary to increase the capacity of the backup batteries for communication facilities in the case of power outages. However, space limitations may make it difficult to install additional lead-acid battery systems in communication buildings and data centers in urban areas. Furthermore, backup battery systems are insurance against quality of the services and do not contribute to a daily income like communication equipments do, so it is desirable that they are as compact as possible. Li-ion batteries have high-energy density, so promise a major contribution to compactness instead of conventional lead-acid batteries in communication power supplies.

Considering the replacement of existing lead-acid batteries by Li-ion batteries, large-capacity Li-ion cell is essential. This is because communication backup systems involve several hundred or several thousand ampere hour batteries and the reduction of

* Corresponding author. Tel.: +81 3 5907 6332; fax: +81 3 5961 6424.
E-mail addresses: tsujik25@ntt-f.co.jp (T. Tsujikawa), yabuta22@ntt-f.co.jp (K. Yabuta), arakawa@ntt-fsoken.co.jp (M. Arakawa), k.hayashi@shinkobe-denki.co.jp (K. Hayashi).

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space losses lead by integration of cells is quite effective to realize compact battery systems. Large-capacity Li-ion cell is also essential to increase the reliability of battery systems, because one can reduce a number of cells and accompanying protective devices. Therefore, we have developed 200-Ah Li-ion cells to replace the lead-acid battery as the next generation of communication power supply backup [1–5].

Because the Li-ion battery has very high-energy density, heat generation in the cell under abnormal conditions such as overcharging or internal short circuit can, in the worst case, result in dangerous thermal runaway. This safety problem is more severe in large-capacity cells. Thermal runaway causes when heat generation is larger than heat diffusion which becomes more difficult in large-capacity cells. This is because surface area of the cell does not increase proportionally to capacity increase. In the backup power supply of a communication system, many cells connected in series and in parallel are maintained in a standby state which is almost fully charged by constant voltage charging ("float charging"). High level of safety must be ensured if large-capacity Li-ion cells are used in the system.

Flame resistant electrolytes are classified as organic electrolyte containing flame retardant, flame-retardant polymer electrolyte [6], inorganic solid electrolyte [7], and ionic liquid. Consequently, we have studied and reported about electrolytes having a self-extinguishing property by containing a phosphazene flame retardant to existing flammable electrolytes [1], because of their current research and commercialization level, availability, low cost, results as flame retardants for plastics [8] and have high-voltage resistance.

In this work, we report the result of several safety tests on developed 200-Ah Li-ion cells and batteries. The tests are based on UN manual of test and criteria (5th revised edition, PIII, 38.3), tests and requirements of safety for secondary lithium cells and batteries, for industrial application (SBA S1101) and tests assumed for telecommunications backup use.

We have also developed Li-ion battery systems using the 200-Ah Li-ion batteries for telecommunications power supply backup. To preserve the performance of Li-ion batteries and safety of them, we have also developed BMS for telecommunications power supply backup. To prevent an overcharge and maintain the voltage of each cell within a fixed range in the module during float charging, a voltage adjustment method in which the charge of a high-voltage cell is consumed by a connected resistance was adopted [9]. Moreover, a voltage adjustment method in which the charger is connected with each cell in the module was proposed [10–12]. In this work we also report the results of tests about the BMS for one year.

2. Large-capacity Li-ion battery safety evaluation

2.1. 200-Ah Li-ion cell fabrication

Mixed solvent of ethylene carbonate with dimethyl carbonate containing a phosphazene flame retardant was used for electrolyte as previously reported [1]. The phosphazene flame retardant has the molecular structure shown in Fig. 1. In the figure, R is aryl group. Lithium manganese oxide spinel in which some of the manganese was replaced with magnesium was used for cathode active material and carbon-coated graphite was used for anode active material [3].

To reduce the dead space of the installation as much as possible, the battery shape was designed to be prismatic (12 kg, 5 L). The discharge characteristic depending on current is shown in Fig. 2. The cell exhibits a good discharge rate characteristic from 0.1 CA to 1.5 CA.

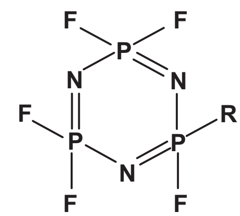

Fig. 1. Molecular structure of the phosphazene flame retardant.

2.2. Safety evaluation

The safety evaluation items for the 200-Ah Li-ion cell and battery were selected as shown in Table 1 on the basis of the risks that can occur in the cell-phone base station or the communication building at NTT while referring to "Recommendations on the Transport of Dangerous Goods: Model Regulations Sixteenth revised edition, Manual of Tests and Criteria Fifth revised edition" (UN) and "Tests and requirements of safety for secondary lithium cells and batteries, for industrial application SBA S 1101″ (Battery Association of Japan).

2.2.1. Altitude simulation

The cell was preserved for 6 h by the pressure of 11.6 kPa or less at 20 ± 5 °C under the assumption of transportation under low pressure. In the results, neither the electrolyte leakage nor the voltage drop was observed.

2.2.2. Thermal cycling

To evaluate the cell sealing and the connection reliability, the cell was heated at 75 ± 2 °C (6 h) and cooled at −40 ± 2 °C (6 h) alternately ten times. Then it was preserved for 24 h at 20 ± 5 °C. In the results, neither the electrolyte leakage nor the voltage drop was observed.

2.2.3. Vibration

The cell was vibrated for 15 min 12 times in X, Y, Z directions, assuming transportation by a track. The frequency was swept from 7 Hz to 200 Hz and then back to 7 Hz again. In the results, neither the electrolyte leakage nor the voltage drop was observed.

2.2.4. Shock

The cell was shocked by the sine half wave, which is 11 s wide and 50-gn peak acceleration. The shock was added three times in X, Y, Z forward directions and backward directions. In the results, neither the electrolyte leakage nor the voltage drop was observed.

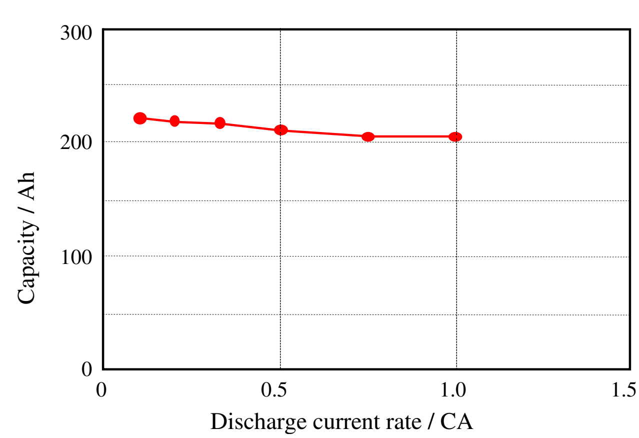

Fig. 2. 200-Ah Li-ion cell discharge characteristic.

Table 1
Safety test items and results.

Test	Test condition			Results	Ref.
	SOC	Temp.	Method		
Altitude simulation	100%	20 ± 5 °C	A cell is stored at a pressure of 11.6 kPa or less for at least 6 h	No leakage, No voltage drop more than 10%	UN
Thermal test	100%	20 ± 5 °C	A cell is stored for 6 h at 75 ± 2 °C followed by storage for 6 h at -40 ± 2 °C. This procedure is repeated for 10 cycles.	No leakage, No voltage drop more than 10%	UN
Vibration	100%	20 ± 5 °C	A cell is vibrated by a sinusoidal waveform with a logarithmic sweep between 7 Hz and 200 Hz and back to 7 Hz traversed in 15 min. This cycle is repeated 12 times for X, Y, X directions.	No leakage, No voltage drop more than 10%	UN
Shock	100%	20 ± 5 °C	A cell is subjected to a half-sine shock of peak acceleration of 50-gn and pulse duration of 11 msec. A cell is subjected to 3 shocks in the positive direction followed by 3 shocks in the negative direction of X, Y, Z directions.	No leakage, No voltage drop more than 10%	UN
External terminal short	100%	25 ± 5 °C	Positive and negative terminals of a cell are connected with a circuit load having resistance of about 0.03 Ω.	No hazard	SBA
Catching fire (1)	100%	25 ± 5 °C	Thermal runaway of a cell in a 13-cell module occur	No chain of thermal runaway	SBA
Catching fire (2)	100%	25 ± 5 °C	A cell neighboring an electric heater is overcharged until the safety valve opens.	No thermal runaway by catching fire	Original
Thermal abuse	100%	25 ± 5 °C	A cell is heated up to 85 °C at the rate of 5 °C min^{-1} and is stored at 85 °C for 3 h.	No hazard	SBA
Overcharge	100%	25 ± 5 °C	A cell is overcharged at 40 A up to 5 V and kept at 5 V for 24 h.	Venting with minor leakage	SBA modified
Over-discharge	0%	25 ± 5 °C	A cell is discharged from SOC0% at 70 A for 3 h.	No hazard	SBA modified
Free fall (1)	100%	25 ± 5 °C	A cell is dropped 3 times from a height of 10 cm.	No leakage, No voltage drop	SBA
Free fall (2)	0%	25 ± 5 °C	A cell is dropped 1 times from a height of 3 m.	No leakage	Original
Nail insertion	100%	25 ± 5 °C	A cell is penetrated by a 2.5-mm diameter nail down to a depth of 72 mm.	Venting with fumes	Original
Burning	100%		A 12-cell module is burned for 1 h.	No explosion, No spread of fire	Original

UN: Recommendations on the Transport of Dangerous Goods: Model Regulations Sixteenth revised edition, Manual of Tests and Criteria Fifth revised edition.
SBA: Tests and requirements of safety for secondary lithium cells and batteries, for industrial application (SBA S1101).

2.2.5. External short circuit

In this test, the cell was assumed to be short-circuited between positive and negative terminals by constructors and maintenance men making mistakes with a metallic tool. The fully charged (SOC 100%) cell terminals were connected with a 30-mΩ conductor. Moreover, the cell was short-circuited by the switch that had been set up in wiring. As a result, the short circuit maximum current flowed for a few minutes, the cell voltage dropped to 0 V. Though the short circuit condition was kept for 6 h, thermal runaway did not occur afterward.

2.2.6. Catching fire (1)

The Li-ion battery module consists of 13 200-Ah Li-ion cells connected in series. To confirm whether thermal runaway occurring in only one cell in the module neither affects other cells nor destabilizes the module, thermal runaway of one cell in the module occurred under compulsion and its influence was examined. Only one cell suffered thermal runaway, and it did not affect other cells.

2.2.7. Catching fire (2)

The catch fire test was carried out assuming the Li-ion cell was set alight by a neighboring ignition source. To simulate the state in which the electrolyte and its mist gush from an opened safety valve when the cell temperature rises due to some reasons, the fully charged (SOC 100%) Li-ion cell was overcharged with 0.5 CA (100 A). And an electric heater that was assumed to be the fire point was set up in the cell neighborhood. The safety valve opened immediately after the test began by the elevation of internal pressure, and the gushed electrolyte and its mist caught fire from the neighboring electric heater. Afterward, the flame around safety valve was gradually extinguished, and thermal runaway did not occur.

2.2.8. Thermal abuse

Because room temperature during summer is assumed to become 50 °C or more in narrow spaces such as the cell-phone base stations, a thermal abuse test was performed in which the Li-ion battery was simulated to be preserved in a high-temperature environment for a long time. The preservation temperature was 85 °C. The fully charged (SOC100%) Li-ion cell was set in thermostatic chamber and heated up at 5 °C per minute. After the cell temperature had reached 85 °C, the state was maintained for 3 h. No abnormality of cell voltage or temperature was observed, and thermal runaway did not occur.

2.2.9. Overcharge

In Li-ion cells, over-charge condition is very dangerous. This is because cell temperature increased by chemical and electrochemical reactions during overcharge in which flammable gas may generate by decomposition of electrolyte, lithium metal may deposit on the anode and oxygen may release from cathode by structural destabilization. Therefore, cutoff circuit is usually involved in BMS of batteries to disconnect them from charger when

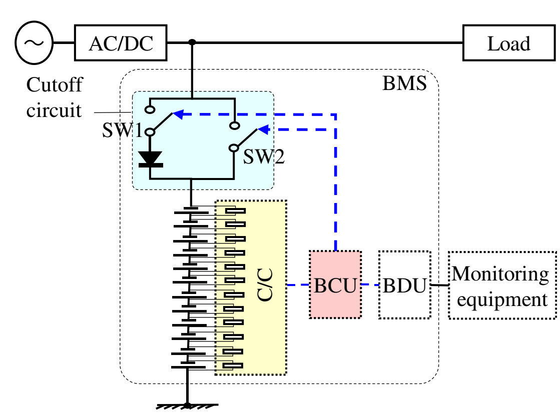

Fig. 3. Battery management system on figuration.

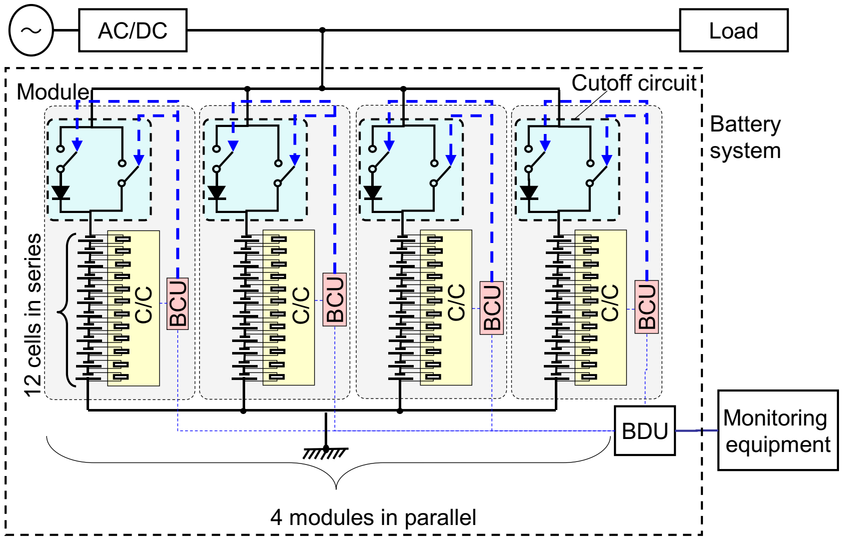

Fig. 4. Configuration for Li-ion battery system.

they are overcharged. The over-charge test was performed under the assumption that the cutoff circuit broke down and the battery was overcharged for a long time. The fully charged (SOC100%) Li-ion cell was charged for 24 h at a constant voltage of 5 V (120% of upper limit) and a maximum current of 0.2 CA (40 A). After the charge began, the cell temperature rose to 92 °C and the cell voltage reached 5 V. Then the safety valve opened when the amount of the overcharge reached 40%, and after that the cell temperature decreased. Thermal runaway did not occur during charging for 24 h.

2.2.10. Over-discharge

The cutoff circuit also operates when the battery module is over-discharged and the battery module is disconnected from a load. The over-discharge test was performed under the assumption that the cutoff circuit broke down and the battery module was extremely over-discharged. The fully discharged (SOC0%) Li-ion cell was connected with a regulated power supply and discharged for 3 h at constant current 0.33 CA (70 A). In the results, the cell voltage dropped 0 V about 30 min later, and its temperature rose to 53 °C. However, venting and thermal runaway did not occur.

2.2.11. Free fall

A free fall test was performed in which the Li-ion cell was assumed to be dropped by mistake during installation or transportation. The fully charged (SOC100%) Li-ion cell was dropped bottom side down three times from a height of 10 cm. The results confirmed no abnormality of battery voltage or temperature after free fall. Moreover, thermal runaway and electrolyte leakage did not occur. Moreover, the fully discharged (SOC0%) Li-ion cell was dropped bottom side down, wide sidewall down, and narrow sidewall down from a height of 3 m one time each. In the results, explosion and electrolyte leakage did not occur.

2.2.12. Nail insertion

A 2.5-mm diameter nail was inserted to a fully charged (SOC 100%) cell down to a depth of 72 mm, which is half the depth of the

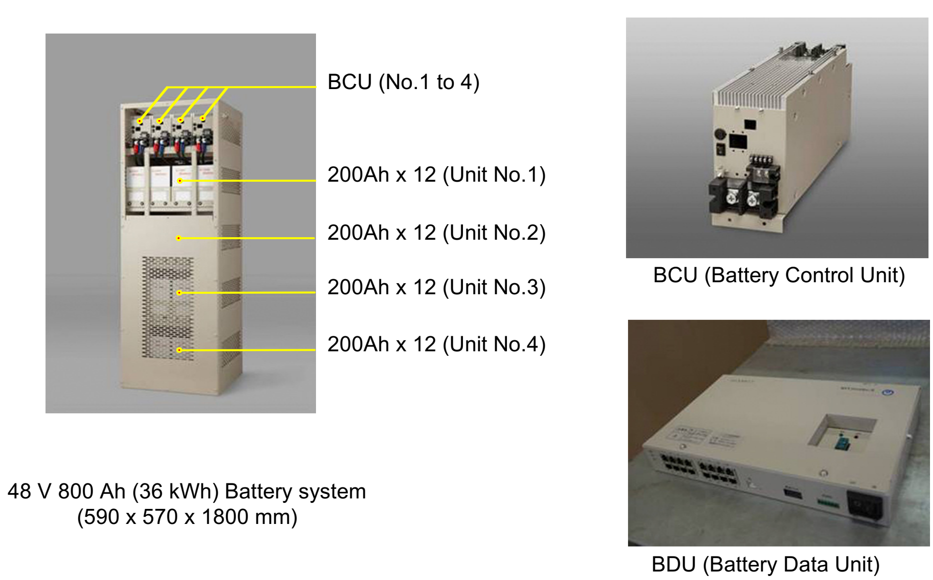

Fig. 5. Li-ion battery system.

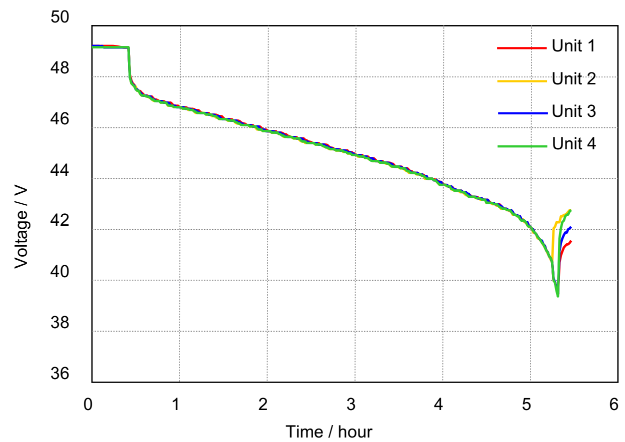

Fig. 6. Discharge test result of battery system.

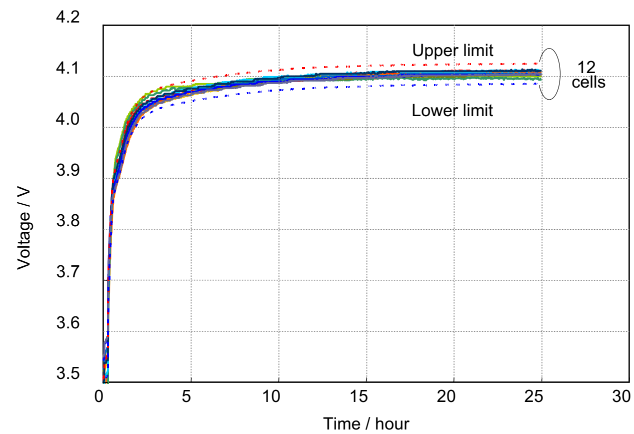

Fig. 8. Cell voltage adjustment function test.

cell. The cell was short-circuited by nail insertion and cell voltage dropped to 0 V slowly. There was no explosion or ignition, though a mild thermal runaway occurred, the internal pressure rose, the safety valve opened, and white smoke was vented. The maximum temperature of the cell outside was about 350 °C.

2.2.13. Burning

A burning test was performed in which the Li-ion battery module was assumed to be set alight by a fire in the communication building or the cell-phone base station. The battery module consisting of 12 fully charged cells and BMS was burned for 1 h. Though safety valves of all cells opened 30 min after the test had started, the cells and module did not explode and fire did not spread.

3. Evaluation of Li-ion battery system

3.1. Battery management system (BMS)

The developed BMS comprises a cell controller (C/C), battery control unit (BCU), cutoff circuit, and battery data unit (BDU). Fig. 3 illustrates the connection and use of the BMS in a telecommunication DC power supply system. The C/C unit has a voltage adjustment circuit for each cell in parallel. BCU is logic circuit which watches the state of cells and modules, and controls charge, discharge, safety. Cutoff circuit cutoffs modules when BCU recognized unsafe state. BDU is interface of BCU and watching system. It transfers the cell data and alarms to the watching system through LAN. The main functions of the BMS are described below.

3.1.1. Cell voltage adjustment function (C/C)

This uses the voltage adjustment circuit connected to each cell to adjust the voltage of each cell of the battery within a fixed voltage range (mean voltage ±20 mV). The voltage adjustment circuit is shunt resistor. The cut-off circuit includes a diode that stops in-flow of current from charger and two switches. This circuit monitors the voltage on each cell, and when the voltage reaches preset value, the charging current is made to bypass that cell via the voltage adjustment circuit set in parallel with the cell. As a result, the cell voltage can be prevented from rising.

3.1.2. Cell protection function (cutoff circuit, C/C and BCU)

When excessive charge is detected, the cutoff circuit (SW2) operates to disconnect the battery module from the system to prevent battery over-charging. At this time the module (12 cells connected in series) is still connected with load. When excessive discharge current or a cell voltage below the nominated value is detected, the cutoff circuits (SW1 and SW2) operate to disconnect the battery module from the system. This prevents battery over-discharging.

3.1.3. Remote monitoring function (BCU and BDU)

This sends alarm and operation data from the BDU to the monitoring center via a LAN. It can also confirm operating information at any time upon request from the monitoring center. In this way, the same remote monitoring functions provided by a conventional VRLA system are implemented.

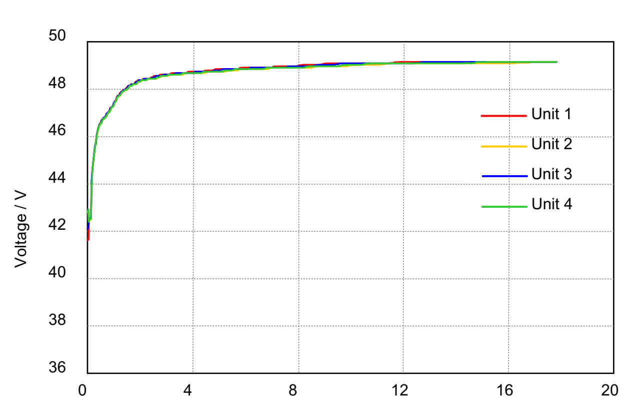

Fig. 7. Charge test result of battery system.

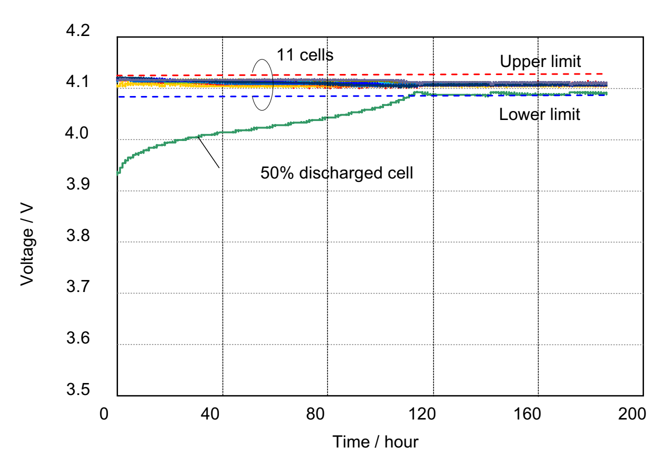

Fig. 9. Cell voltage adjustment function test (include SOC50% cell).

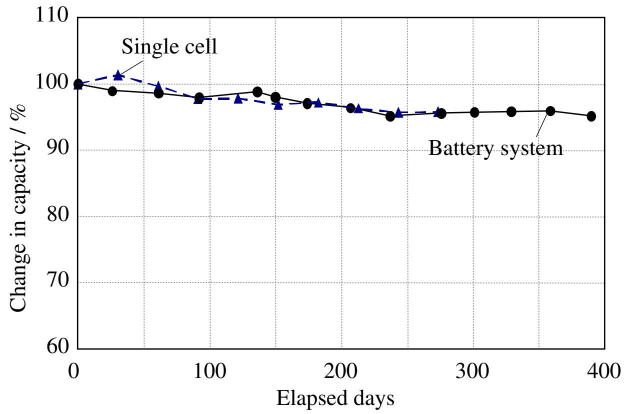

Fig. 10. Capacity transition of the battery system.

3.2. Composition of battery system

Under the assumption of application to DC power sources for communication equipment, 12 cells in series serve as a basic unit (module). To achieve higher voltages by series connection of these modules, a single BCU can accommodate up to 10 C C^{-1} units. Battery capacity is increased by use connected in parallel (up to 15).

3.3. System experiments

We constructed an experimental 36-kWh battery system with four 200-Ah Li-ion battery modules and the BMS that we fabricated. Fig. 4 shows the system configuration. The battery system, the BCU, and the BDU are shown in Fig. 5. Four battery modules were installed in parallel in one rack. Four BCUs that include a cutoff circuit were also installed in the upper part of the rack.

3.3.1. Charge and discharge test

To confirm the charge and discharge performance of the battery system, the charge and discharge test was performed. The fully charged battery system was discharged at 0.2 CA, and then charged at a constant voltage of 49.2 V and a maximum current of 0.2 CA. The test results are shown in Figs. 6 and 7. The results confirm there was no overcharge, no over-discharge, and the discharge and charge characteristics of each module were almost the same.

3.3.2. Cell voltage adjustment function test

To confirm the cell voltage adjustment function of the C/C, the charge and discharge test was performed. Fig. 8 shows each cell voltage of module No.1 during the recovery charge performed in 3.2.1. Each cell voltage was adjusted within the target voltage range (mean voltage ±20 mV) by the C/C. Next, hot-swapping test which is very important for maintenance of backup system was carried out. One cell in module No.1 was cutoff from the module and discharged down to 50% of the nominal capacity at 0.2 CA. The other 11 cells maintained the full charge. Afterward, the discharged cell was inserted to the module which was in float-charging. Fig. 9 shows the results. Even when the low state of charge cell existed in a battery module, the voltage of each cell of the module was adjusted to within a fixed voltage range by C/C. Hot-swapping test was also carried out on modules. Namely, a discharged module down to 50% SOC was inserted to the battery system which was in float charging. Swapped module is well controlled by BMS to reach the float-charging condition.

3.3.3. Long-term operation test

The system was operated for about 400 days in a state of floating charge. Moreover, the battery system was discharged every month to check the capacity. The capacity transition of the battery system is shown in Fig. 10. The capacity change of a single cell is additionally shown for comparison. The system and a single cell performed very similarly. More than 95% of initial capacity is obtained after 400 days float charging.

4. Summary

To be used as a backup power supply for telecommunications, the Li-ion battery requires high safety and high reliability. Safety tests of large-capacity Li-ion cell were performed assuming the communications power supply backup. In addition, the Li-ion battery system consisting of battery modules and BMS was evaluated. Consequently, the following results were found.

1) The safety tests were performed based on the risks that can occur in the cell-phone base station or the communication building at NTT. The results showed there was no explosion, ignition, or thermal runaway. Therefore, flame retardant containing 200-Ah cell was significantly improved in safety.
2) The 36-kW Li-ion battery system consisted of the developed 200-Ah Li-ion battery modules and Li-ion BMS. Then evaluation tests were performed. The results showed the BMS battery management function operates well, adjusting the voltage of each cell to within the target voltage (mean voltage ±20 mV). The system was operated for about 400 days in a state of floating charge. More than 95% of initial capacity is obtained after 400 days float charging. Hot-swapping tests of a cell or a module, which are 50% in SOC, are also performed assuming maintenance of the backup system. Swapped cell or module is well controlled by BMS to reach the float-charging condition.

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